The Direct Determination of Oxygen by Hydrogenation

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

PAUL MILLER GOODLOE 2nd

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To my aunt

Miss Jane F. Goodloe

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Direct Determination of Oxygen in Organic Compounds by Hydrogenation

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RUSSELL and Fulton (*8*) and Russell and Marks (*9*) reported an improved method for the direct determination of oxygen in organic compounds containing only carbon, hydrogen, and oxygen and in compounds also containing nitrogen. Later Marks (*4*) applied the method to the determination of total oxygen in oxidized oils in the presence of small amounts of sulfur contained in the oils. The method is the hydrogenation method of ter Meulen (*7*); it has enjoyed the best success of all the direct methods for oxygen, although some workers have reported difficulties with it, one of the latest being Gauthier (*2*). It seemed desirable to render the method more dependable and capable of wider application.

With the present procedure and apparatus it has been successfully applied, without any modifications, to a similar variety of compounds containing carbon, hydrogen, oxygen, nitrogen, and sulfur. Moreover, the reproducibility was found to be generally as good as the accuracy—that is, about 0.1 per cent for the oxygen.

Apparatus

The apparatus of Russell and Fulton (*8*) was modified only slightly (Figure 1).

The cracking, 6, and catalyst chambers, 7, and preheater, 2, were electrically heated by specially prepared furnaces each 20 cm. long. A 2.5 × 5 × 10 cm. (1 × 2 × 4 inch) cast-aluminum block, 5, with a groove along the center of a large face and a longitudinal hole for a thermometer, was used in vaporizing the sample. A glass mortar, 8, 8 cm. long in which toluene was refluxed to maintain a temperature of 111° C. was used to heat a 2-cm. plug of silver sulfate in the case of halogen-containing compounds. This silver sulfate was omitted in all runs where halogen was not involved.

A capillary stopcock, 1, was used to adjust the flow of hydrogen; the hydrogen was dried by sodium hydroxide pellets, 3, and anhydrous calcium sulfate, 4, and was delivered to the apparatus under a pressure of about 2 meters (6 feet) of water siphoned from one 19-liter (5-gallon) carboy to another. The water formed

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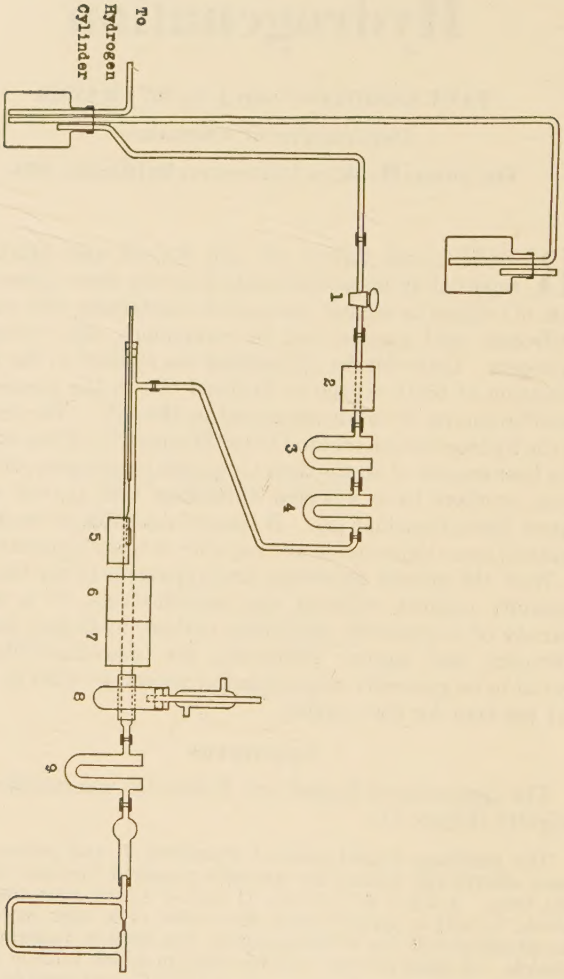


FIGURE 1. DIAGRAM OF APPARATUS

during the analysis was absorbed by anhydrous calcium sulfate contained in a 150-mm. Schwartz U-tube, 9, attached to the quartz tube by a rubber connection. The exit hydrogen was passed through a flowmeter, 10, open to the atmosphere. The clear quartz tube had a total length of 70 cm. and an internal diameter of 7 mm.

The means employed for the introduction of the regular platinum microboat, during an exit flow of hydrogen of more than 200 cc. per minute, is illustrated in Figure 2. A one-hole rubber stopper contained a solid glass rod which extended into the quartz tube about 10 cm. Sealed into the end of this rod was a double length of Nichrome wire having a loop on the end the right size and shape for the microboat to fit snugly. The rod and wire remained in the tube during the analysis and attendant vaporization of the sample. The boat was removed by pulling it to the end of the quartz tube with the rod and wire and then picking it up with clean forceps. The boat containing the next sample was immediately placed in the wire loop and pushed into place in the tube.

Catalyst and Cracking Surface

The nickel chromite catalyst is quickly prepared from readily available materials and is easily handled even after reduction. The freshly prepared catalyst, after reduction at 400° C. for 10 or 12 hours (overnight) and then at operating temperatures for 1 hour, gave a constant blank of about

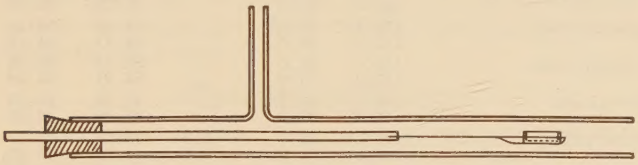


FIGURE 2. INTRODUCTION OF MICROBOAT

0.2 mg. per liter of hydrogen. Russell and Fulton (*8*) reported that it took 2 or 3 days to reduce their thoriapromoted nickel catalyst to a point where it gave a similar constant blank.

Of especial significance is the fact that the activity of the nickel chromite catalyst is unaffected by sulfur (*3*) up to relatively large amounts, and as sulfur is completely retained by this substance (*3*) the method is applicable to sulfur-containing compounds. Marks (*4*) has shown that the thoria-promoted nickel catalyst is also resistant to poisoning by sulfur.

Nickel chromite was also found to make the best cracking surface when heated to red heat. Some carbon dioxide escaped when platinized quartz beads were tried as cracking surface with nickel chromite as catalyst, whereas when nickel chromite was used as cracking surface (at 750° C.) and as catalyst (at 400°) the carbon dioxide was completely hydrogenated. Under these conditions the nitrogen in nitrogen-containing compounds is cracked directly to free nitrogen and practically no ammonia is formed (Table I).

The catalyst was prepared by weighing 31 grams of ammonium chromate [$(NH_4)_2CrO_4$] into one beaker and 29 grams of nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] into another; the nickel nitrate was dissolved in 50 cc. of distilled water and the solution poured over the dry ammonium chromate with stirring. This produces the double salt, $NiCrO_4 \cdot (NH_4)_2CrO_4 \cdot 6H_2O$ (*1*). After about 10 minutes of stirring, the precipitate was filtered off with suction, dried over a low flame, and decomposed in small portions in a porcelain casserole over a Bunsen burner at 200° C. with stirring.

$$NiCrO_4 \cdot (NH_4)_2CrO_4 \cdot 6H_2O = Ni(CrO_2)_2 + N_2 + 10H_2O$$

The catalyst so obtained was in fluffy particles which were put directly into the quartz tube for a distance of 40 cm. and into the preheater tube and packed slightly with light tapping. Approximately 10 grams of the catalyst were used in the combustion tube and 5 grams in the preheater.

TABLE I. DETERMINATION OF OXYGEN

Substance	Sample	Water	Ammonia	Oxygen	
				Found	Calculated
	Mg.	*Mg.*	*Mg.*	%	%
Benzoic acid	81.2	23.9	...	26.14	26.22
	99.2	29.3	...	26.23	26.22
Succinic acid	110.8	67.5	...	54.11	54.21
	112.6	68.6	...	54.11	54.21
Tartaric acid	110.6	37.6	...	30.19	63.96
	117.9	47.0	...	35.41	63.96
Picric acid	46.7	25.7	...	48.88	48.89
	60.2	33.0	...	48.69	48.89
3,5-Dinitrobenzoic acid	102.1	52.0	0.5	45.23	45.27
	101.6	51.8	0.6	45.28	45.27
Urea	89.5	26.8	0.2	26.60	26.64
	88.1	26.5	0.0	26.71	26.64
Acetamide	83.2	25.4	0.0	27.12	27.09
	82.2	25.0	−0.5	27.01	27.09
	88.5	27.0	0.7	27.09	27.09
	77.9	23.7	0.0	27.02	27.09
Trinitrobenzene	62.434	31.748	...	45.17	45.06
	65.278	33.032	...	44.94	45.06
	51.551	26.144	...	45.05	45.06
Pyrrol derivative ($C_{10}H_{12}NO_3$)	45.202	12.160	...	23.89	24.60
	63.962	17.683	...	24.55	24.60
	62.062	17.116	...	24.50	24.60
Diphenyl sulfone	70.1	11.5	...	14.57	14.67
	76.5	12.6	...	14.63	14.67
	68.2	11.2	...	14.58	14.67
	71.2	11.8	...	14.72	14.67
Chloroacetic acid	135.6	55.7	...	36.48	33.87
	127.6	54.7	...	38.08	33.87

Procedure

In general, the procedure of Russell and Fulton was followed. Fifty minutes were allowed for a run: 20 minutes for the vaporization of the sample, and 30 minutes for sweeping out the tube. The rate of flow of hydrogen was 60 cc. per minute.

The most important and by far the most difficult part of the analysis is the vaporization of the sample, which should be done slowly and evenly by heating the aluminum block under

the sample with a microburner. A thermometer in the block registers the approximate temperature of the sample and a practice run is often advisable to learn the peculiarities of the individual substance when volatilized; the vaporization of the sample should be conducted about 20° above its melting point the first time it is run.

Substances will distill from the hot to the cold portion of the tube and in many cases distillation countercurrent to the flow of hydrogen was observed. This is effectively prevented by keeping the tube hotter (with an oxygen blowtorch) 6 or 8 cm. preceding the sample than in the region surrounding the boat. When all the substance has been volatilized from the boat, the aluminum block should be lowered and the boat heated with the free flame from the microburner before the oxygen blowtorch is applied.

With picric acid (Table I), when easily decomposable or explosive substances are used, it was found necessary to keep the temperature of the sample as low as possible during the vaporization and to spend a longer time than usual on this process. It is advisable to increase the rate of flow of the hydrogen to at least 90 cc. per minute.

With diphenyl sulfone (Table I), when difficultly decomposable substances are analyzed it is necessary to slow the rate of flow down to about 30 cc. per minute, so that the vapors may remain in contact with the cracking surface for a longer period of time.

Discussion of Results

In the case of compounds containing only carbon, hydrogen, and oxygen the results were satisfactory with one exception: with tartaric acid the percentage of oxygen found was very much too low. This was true for another hydroxy compound, sucrose, the results for which were thrown out because of an inactive catalyst.

It seems impossible to vaporize either tartaric acid or sucrose without carbonization of most of the sample. Other substances will carbonize, but when they are heated in the full blast of the oxygen blowtorch all the oxygen is given up and the results are satisfactory. In the case of sucrose, test runs with benzoic acid proved that the catalyst was inactive at the time of the sucrose runs. This may also be true for tartaric acid, though it is believed that all the oxygen was not volatilized from the residue in the boat. However, Gauthier (*2*) reported a successful analysis of this substance.

In a private communication, W. R. Kirner stated his inability to get satisfactory results with sucrose by a microhydrogenation method using a thoria-promoted nickel catalyst, and preliminarily attributed his consistently low results to difficulty in volatilizing all the oxygen from the sample. Russell and Fulton (*8*) reported the successful analysis of sucrose by hydrogenation.

Since nickel chromite catalyst will withstand fairly large quantities of sulfur, analyzing tartaric acid and sucrose mixed

with a little free sulfur in the boat is planned in an effort to displace all the oxygen.

No difficulties were encountered with the compounds containing nitrogen; however, the polynitro derivatives are so explosive that they are difficult to handle.

Table I also shows the outcome of an attempt to determine the amount of ammonia formed in the case of 3,5-dinitrobenzoic acid, urea, and acetamide. An absorption tube containing glass wool moistened with concentrated sulfuric acid was attached following the tube containing calcium sulfate. No appreciable amount of ammonia was formed in any case. This is in agreement with the findings of ter Meulen (*5*), although Russell and Marks (*9*) reported considerable, though not theoretical, amounts of ammonia.

Although diphenyl sulfone was the only sulfur-containing compound tried, it is believed to be a sufficient test of the method. With this substance it was demonstrated that sulfur in reasonable amounts does not poison the catalyst completely.

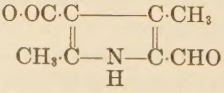
Halogen compounds (chloroacetic acid) cannot be successfully analyzed with nickel chromite catalyst prepared as directed. This is in agreement with ter Meulen's findings (*6*) that a thoria-promoted catalyst is attacked by halogen acid, liberating water from the thorium oxide present. The chromite catalyst prepared according to the method outlined contains a small amount of free oxide, which presumably is never completely reduced.

The introduction of a slight modification should make the method applicable to halogen-containing compounds when nickel chromite is used. When this catalyst is pure it is insoluble in boiling concentrated hydrochloric acid (*3*), so that if the catalyst, as prepared with a small excess of chromic oxide, were boiled or leached with several portions of boiling hydrochloric acid, it should no longer react to produce water under operating conditions in the quartz tube. Preliminary results from work now in progress indicate this to be true.

It has been shown definitely (Table I) that ammonia is not formed in the presence of this catalyst, even from a substance like urea; it is therefore planned to use phosphorus pentoxide as the absorbent for water, with no silver sulfate in the tube when analyzing halogen compounds. It is then possible that halogen may be determined simultaneously.

With these two modifications, the leaching of the catalyst with hydrochloric acid and the substitution of phosphorus pentoxide for calcium sulfate as the absorbing agent for water, it is believed the method will be readily applicable to halogen-containing compounds and therefore general with one simple setup.

The pyrrol derivative



and the trinitrobenzene, furnished by A. H. Corwin, were run as unknowns for Frazer; a Kuhlmann microbalance was used for these runs with no modification of apparatus or procedure except the use of micro absorption tubes weighing about 15 grams when filled.

Summary

The method of hydrogenation has been successfully employed for determining the percentage of oxygen in organic compounds containing carbon, hydrogen, oxygen, nitrogen, and sulfur, using an active nickel chromite catalyst at 400° C. The low results obtained in the analysis of tartaric acid and sucrose indicated extreme difficulty in driving all the oxygen from the residue in the boat.

The accuracy and reproducibility are each about 0.1 per cent for the oxygen, or about that with which carbon is determined in ordinary combustions, and the apparatus and procedure are almost as simple as for combustions. The time allotted to a single run was 50 minutes.

A modification has been suggested which will probably make the method applicable to halogen-containing compounds.

Acknowledgment

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Literature Cited

(1) Briggs, *J. Chem. Soc.*, **83**, 394 (1903); **85**, 678 (1904); **1929**, 242.
(2) Gauthier, *Bull. soc. chim.*, (5) **2**, 322 (1935).
(3) Jackson, Ph.D. thesis, The Johns Hopkins University, 1934.
(4) Marks, IND. ENG. CHEM., Anal. Ed., **7**, 102 (1935).
(5) Meulen, ter, *Rec. trav. chim.*, **43**, 899 (1924).
(6) Meulen, ter, *Ibid.*, **53**, 118 (1934).
(7) Meulen, ter, and Heslinga, "Neue Methoden der organisch-chemischen Analyse," Leipzig, Akademische Verlagsgesellschaft, 1927.
(8) Russell and Fulton, IND. ENG. CHEM., Anal. Ed., **5**, 384 (1933).
(9) Russell and Marks, *Ibid.*, **6**, 381 (1934).

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AUTOBIOGRAPHY

Paul Miller Goodloe, 2nd, was born at Berea, Kentucky, May 21, 1911. He was graduated from the Madison High School, Richmond, Kentucky, in 1927 and entered the University of Kentucky, Lexington, that fall as an engineering student. After one year he took up a pre-medical course and at the end of three years returned to Richmond, Kentucky, to the Eastern Kentucky Teachers College to major in Chemistry. He was graduated from the latter institution in August, 1932.

The school year 1932–33 he spent as a student assistant in Chemistry at the University of Tennessee, Knoxville, and in the fall of 1933 entered the School of Higher Studies, Faculty of Philosophy, the Johns Hopkins University, Baltimore, Maryland, as a candidate for the degree of Doctor of Philosophy.